

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 869 267 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
07.10.1998 Bulletin 1998/41

(51) Int. Cl.⁶: F02D 41/14, F01N 3/08

(21) Application number: 98106083.3

(22) Date of filing: 02.04.1998

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 03.04.1997 JP 85294/97

(71) Applicant:
TOYOTA JIDOSHA KABUSHIKI KAISHA
Aichi-ken 471-8571 (JP)

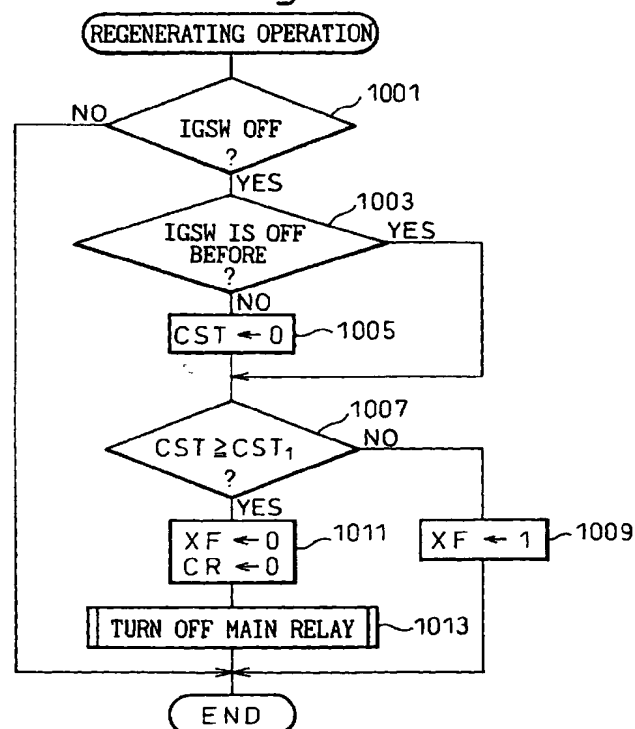
(72) Inventors:
• Gotoh, Masato
Toyota-shi, Aichi (JP)
• Katoh, Kenji
Toyota-shi, Aichi (JP)
• Asanuma, Takamitsu
Toyota-shi, Aichi (JP)

(74) Representative:
Leson, Thomas Johannes Alois, Dipl.-Ing. et al
Patentanwälte
Tiedtke-Bühling-Kinne & Partner,
Bavariaring 4
80336 München (DE)

(54) An exhaust gas purification device for an internal combustion engine

(57) The exhaust gas purification device includes a NO_x absorbent disposed in an exhaust gas passage of an internal combustion engine. The engine is mainly operated at a lean air-fuel ratio. The NO_x absorbent absorbs NO_x in the exhaust gas from the engine when the exhaust gas flowing into the NO_x absorbent is at a lean air-fuel ratio, and releases the NO_x absorbed therein and reduces it when the air-fuel ratio of the exhaust gas becomes a rich air-fuel ratio. A control circuit is provided for controlling the operating air-fuel ratio of the engine. When the ignition switch of the engine is turned off, the control circuit continues the engine operation for a predetermined period before terminating the engine operation. During this engine operation, the operating air-fuel ratio of the engine is controlled at a rich air-fuel ratio to supply exhaust gas with a rich air-fuel ratio to the NO_x absorbent. Therefore, NO_x absorbed and held therein when the ignition switch is turned off is released and reduced by the rich air-fuel ratio exhaust gas from the engine. Since the NO_x absorbent is maintained at the condition where no NO_x remains in the NO_x absorbent after the engine has stopped, unreduced NO_x is not released from the NO_x absorbent even if the NO_x absorbent is cooled after the engine has stopped.

Fig.10



EP 0 869 267 A2



Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an exhaust gas purification device for an internal combustion engine. More specifically, the present invention relates to exhaust gas purification device which includes an NO_x absorbent for removing NO_x in the exhaust gas of an internal combustion engine.

2. Description of the Related Art

An exhaust gas purification device which disposes a NO_x absorbent in an exhaust gas passage of an internal combustion engine is known in the art. A NO_x absorbent absorbs NO_x in the exhaust gas when the exhaust gas from an engine is at a lean air-fuel ratio, and releases the absorbed NO_x and reduces it when the exhaust gas from the engine is at a rich air-fuel ratio. An exhaust gas purification device of this type is, for example, disclosed in international patent publication WO93-25806. In the exhaust gas purification device in the '806 publication, a NO_x absorbent is used for absorbing NO_x in the exhaust gas of a lean-burn engine which can be operated at an lean air-fuel ratio. The device in the '806 publication is provided with means for detecting the amount of the NO_x absorbed in the NO_x absorbent and monitors the amount of the absorbed NO_x during the lean air-fuel ratio operation of the engine. When the amount of the absorbed NO_x reaches a predetermined value, the device lowers the oxygen concentration in the exhaust gas in order to cause the NO_x absorbent to release the absorbed NO_x and reduce the same using reducing substances such as HC, CO in the exhaust gas (in this specification, the operation which causes the NO_x absorbent to release the absorbed NO_x and reduce the released NO_x to N₂ is referred to as "a regenerating operation"). The device in the '806 publication prevents the NO_x absorbent from being saturated with the absorbed NO_x by performing the regenerating operation when the amount of the NO_x absorbed in the NO_x absorbent reaches the predetermined value.

However, in the device of the '806 publication, there is a problem in that the absorbed NO_x may be released from the NO_x absorbent after the engine has stopped and then diffuse into the atmosphere. As explained later, the maximum amount of NO_x which can be absorbed and held by the NO_x absorbent, i.e., a NO_x saturating amount varies depending on the temperature of the NO_x absorbent. Usually, the NO_x absorbent is disposed in the exhaust gas passage at a position where the temperature of the NO_x absorbent falls in a range where the NO_x saturating amount becomes the maximum value (for example, 300°C to 500°C), and the

above-noted predetermined value of the absorbed NO_x at which the regenerating operation is commenced is set at a relatively large value (for example, 70 to 80% of the maximum NO_x saturating amount in the above temperature range). Therefore, if the engine is stopped immediately before the NO_x amount absorbed in the NO_x absorbent reaches the above-noted predetermined value, a substantially large amount of NO_x is held in the NO_x absorbent after the engine has stopped. However, since the temperature of the NO_x absorbent decreases due to heat radiation from the NO_x absorbent after the engine has stopped, the NO_x saturation amount (i.e., the maximum amount of NO_x which the NO_x absorbent can hold) decreases. Therefore, when the NO_x saturation amount becomes lower than the amount actually held in the NO_x absorbent due to the cooling of the NO_x absorbent, the amount of NO_x in excess of the NO_x saturating amount is released from the NO_x absorbent and diffuses into the atmosphere without being reduced. The amount of the NO_x diffusing into the atmosphere increases in proportion to the maximum NO_x saturation amount of NO_x absorbent, i.e., a NO_x absorbing capacity of the NO_x absorbent. Therefore, if the NO_x absorbent having a large NO_x absorbing capacity is used, the amount of NO_x diffused into the atmosphere after the engine has stopped also become large.

This problem may not occur if the above-noted predetermined value of the absorbed NO_x at which the regenerating operation is commenced (hereinafter, referred to as "a regenerating amount") is set at a relatively low value. By setting the regenerating amount at lower value, the maximum amount of NO_x absorbed and held in the NO_x absorbent during the engine operation becomes low. Therefore, if the regenerating amount is set at a sufficiently low level, the amount of NO_x held in the NO_x absorbent when the engine is stopped never exceeds the NO_x saturating amount even if the NO_x saturation amount decreases after the engine has stopped due to the cooling of the NO_x.

However, if the regenerating amount is set at a lower value, the NO_x absorbing capacity of the NO_x absorbent cannot be fully utilized. For example, if the regenerating amount is set at, for example, 20% of the maximum NO_x saturating amount instead of conventional 70 to 80%, the frequency of the regenerating operation during the engine operation increases by roughly three times. When the frequency of the regenerating operation increases, problems such as a deterioration in the driveability due to changes in the operating air-fuel ratio of the engine and a worsening of a fuel economy of the engine may occur. Therefore, the solution by setting the regenerating amount at a lower value is not practical.

SUMMARY OF THE INVENTION

In view of the problems in the related art as set forth above, the object of the present invention is to provide

an exhaust gas purification device which is capable of fully utilizing the NO_x absorbing capacity of a NO_x absorbent without causing unreduced NO_x to be released to the atmosphere after the engine has stopped.

This object is achieved by an exhaust gas purification device for an internal combustion engine which comprises a NO_x absorbent disposed in an exhaust passage of an internal combustion engine, wherein the NO_x absorbent absorbs NO_x in the exhaust gas of the engine when the air-fuel ratio of the exhaust gas flowing into the NO_x absorbent is lean, and releases and reduces the absorbed NO_x when the air-fuel ratio of the gas flowing into the NO_x absorbent becomes rich, and a regenerating means for performing a regenerating operation which causes the NO_x absorbent to release and reduce the absorbed NO_x by supplying a rich air-fuel ratio gas to the NO_x absorbent when the engine is stopped.

According to the present invention, the NO_x absorbent also holds a certain amount of NO_x when the engine is stopped. This amount of NO_x may be large when the NO_x absorbing capacity of the NO_x absorbent is large. Therefore, unreduced NO_x may be released to the atmosphere if the NO_x absorbent is cooled after the engine has stopped. However, according to the present invention, the regenerating means performs the regenerating operation when the engine is stopped and this causes the NO_x absorbent to release the absorbed NO_x and reduce the same. Therefore, when the regenerating operation is completed after the engine has stopped, the amount of NO_x held in the NO_x absorbent becomes low, and the amount of NO_x held in the NO_x absorbent is always kept lower than the NO_x saturating amount even if the NO_x absorbent is cooled after the engine has stopped.

According to the present invention, the NO_x absorbing capacity of the NO_x absorbent can be fully utilized by setting the regenerating amount of the NO_x absorbent at a conventional value while preventing the NO_x absorbent from releasing unreduced NO_x into the atmosphere. This makes it possible to reduce the frequency of regenerating operation by using a NO_x absorbent having a larger NO_x absorbing capacity.

If a NO_x absorbent having sufficiently large NO_x absorbing capacity is used, i.e., if the NO_x absorbing capacity of the NO_x absorbent is larger than a total amount of NO_x released from the engine during the whole engine operation period, the regenerating operation of the NO_x absorbent is not required during the engine operation. However, in this case, the amount of NO_x released from the NO_x absorbent due to cooling becomes large. Further, even if the NO_x is not released from the NO_x absorbent after the engine has stopped, the amount of NO_x held in the NO_x absorbent does not decrease if the regenerating operation is not performed at all. This means that when the engine is restarted, the NO_x absorbent has to start to absorb NO_x in the

exhaust gas in the condition where the amount of NO_x absorbed therein is already relatively high. This may cause the NO_x absorbent to saturate with NO_x during the next operation of the engine.

According to the present invention, this problem also can be solved. Since the NO_x absorbent is regenerated every engine stop, when the engine is restarted, the NO_x absorbent is always capable of starting to absorb NO_x in the condition where the amount of the absorbed NO_x in the NO_x absorbent is very low. This prevents the NO_x absorbent from being saturated with NO_x in the exhaust gas during the engine operation if a NO_x absorbent having a sufficiently large NO_x absorbing capacity. Namely, according to the present invention, the necessity for the regenerating operation of the NO_x absorbent during the engine operation, and the resulting deterioration of the driveability and worsening of the fuel economy, can be eliminated by using a NO_x absorbent having a sufficiently large NO_x absorbing capacity.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be better understood from the description as set forth hereinafter, with reference to the accompanying drawings in which:

Fig. 1 schematically illustrates an embodiment of the exhaust gas purification device according to the present invention when it is applied to an internal combustion engine for an automobile;

Fig. 2 shows an example of a numerical table used in the fuel injection amount calculation;

Fig. 3 shows a typical change in the composition of exhaust gas of an internal combustion engine according to the change in the operating air-fuel ratio of the engine;

Figs. 4A and 4B illustrates a mechanism of an absorbing and releasing operation of a NO_x absorbent;

Fig. 5 illustrates the operating air-fuel ratio of the engine in Fig. 1 during the regenerating operation of the NO_x absorbent;

Fig. 6 illustrates a typical change in the amount of NO_x generated by an internal combustion engine per unit time according to the change in the load conditions of the engine;

Fig. 7 is a flowchart illustrating an example of a calculating (detecting) operation of the amount of NO_x absorbed in the NO_x absorbent in Fig. 1;

Fig. 8 is a flowchart illustrating an example of the regenerating operation of the NO_x absorbent;

Fig. 9 illustrates a typical change in the NO_x saturating amount of the NO_x absorbent according to the change in the temperature thereof;

Fig. 10 is a flowchart illustrating an example of the regenerating operation of the NO_x absorbent which is performed after the engine has stopped;

Fig. 11 is a flowchart illustrating a count up operation of a time counter used in the operation in Fig. 10; and

Fig. 12 schematically illustrates another embodiment of the exhaust gas purification device according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Fig. 1 is a drawing schematically illustrating the general configuration of an embodiment of the present invention when it is applied to an internal combustion engine for an automobile.

In Fig. 1, reference numeral 1 represents an internal combustion engine for an automobile. In this embodiment, the engine 1 is a multi-cylinder type engine, and Fig. 1 shows one of the cylinders of the engine 1.

In Fig. 1, the respective cylinders are provided with a combustion chamber 3, a piston 2, an ignition plug 4, an intake port 6 with an intake valve 5 and an exhaust port 8 with an exhaust valve 7. The intake ports 6 of the respective cylinders are connected to a surge tank 10 by an intake manifold 9 and, on the intake manifold 9, a fuel injection valve 11 is disposed near each intake port 6. The fuel injection valves 11 inject pressurized fuel into the intake port 6 of the respective cylinders.

The surge tank 10 is connected to an intake air filter 14 via an intake air duct 12 and an air-flow meter 13. Numeral 15 represents a throttle valve disposed in the intake air duct 12.

The exhaust ports 8 of the respective cylinders are connected to a common exhaust pipe 17 by means of an exhaust manifold 16. On the exhaust pipe 17, a casing 19 containing a NO_x absorbent 18 is disposed. The NO_x absorbent 18 will be explained later in detail.

Reference numeral 30 in Fig. 1 represents a control circuit of the engine 1. The control circuit 30 consists of, for example, a microcomputer provided with a ROM (read only memory) 32, a RAM (random access memory) 33, a CPU (microprocessor) 34, an input port 35 and an output port 36, which are interconnected by a bi-directional bus 31.

The airflow meter 13 is, for example, a potentiometer-type which generates an analog voltage signal proportional to the amount of air flowing therethrough and drawn into the engine 1. The signal from the airflow meter 13 is transmitted to the input port 35 of the control circuit 30 through an analog-to-digital (A/D) converter 37. Further, pulse signal representing the rotational speed of the engine 1 is transmitted to the input port 35 from a speed sensor 23 disposed near the crankshaft of the engine 1.

The output port 36 is connected to the fuel injection valves 11 and the ignition plugs 4 of the respective cylinders via a drive circuit 39 and an ignition circuit 38, respectively.

In this embodiment, the control circuit 30 calculates the amount of the fuel injection TAU in an fuel injection

amount calculating operation (not shown) based on the formula $TAU = TP \times Kt$, where TP represents a base fuel injection amount and Kt represents a correction factor. The base fuel injection amount TP is an amount of the fuel required to maintain the air-fuel ratio of the air-fuel mixture in the combustion chamber at a stoichiometric air-fuel ratio. The value of the base fuel injection amount TP is determined by, for example, experiment using an actual engine, and is stored in the ROM 32 of the control circuit 30 in the form of a numerical table based on the engine load conditions (such as the amount of intake air per one revolution of the engine, Q/N and engine speed N) as parameters. Fig. 2 shows a typical form of the numerical table used for calculating the base fuel injection amount TP.

The correction factor Kt is used for adjusting the operating air-fuel ratio of the engine (i.e., the air-fuel ratio of the air-fuel mixture supplied to the combustion chambers of the engine 1. When Kt is set at 1.0, the operating air-fuel ratio of the engine becomes the stoichiometric air-fuel ratio. When the correction factor Kt is set at $Kt < 1.0$, the operating air-fuel ratio of the engine becomes higher than the stoichiometric air-fuel ratio, i.e., the engine is operated at a lean air-fuel ratio. On the contrary, when the correction factor Kt is set at $Kt > 1.0$, the operating air-fuel ratio of the engine becomes lower than the stoichiometric air-fuel ratio, i.e., the engine 1 is operated at a rich air-fuel ratio.

In this embodiment, the value of Kt is maintained at, for example, $Kt = 0.7$ in the usual operation of the engine 1 to operate the engine 1 at a lean air-fuel ratio.

Fig. 3 schematically illustrates the changes in the concentrations of O₂ and unburned HC, CO in the exhaust gas in accordance with the change in the operating air-fuel ratio of the engine 1. As shown in Fig. 3, the concentrations of unburned HC and CO increase as the operating air-fuel ratio of the engine becomes rich, and the concentration of O₂ increases as the operating air-fuel ratio becomes lean.

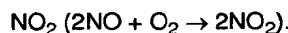
The NO_x absorbent 18 in this embodiment uses, for example, alumina as a carrier and, on this carrier, precious metals such as platinum Pt rhodium Rh and at least one substance selected from alkali metals such as potassium K, sodium Na, lithium Li and cesium Cs; alkali-earth metals such as barium Ba and calcium Ca; and rare-earth metals such as lanthanum La and yttrium Y are carried. The NO_x absorbent 18 absorbs NO_x in the exhaust gas flowing into the NO_x absorbent when the air-fuel ratio of the exhaust gas is lean, and releases the absorbed NO_x When the oxygen concentration of the exhaust gas flowing into the NO_x absorbent becomes lower.

In this specification, the term "air-fuel ratio of the exhaust gas" means a ratio of the amounts of the air and the fuel supplied to the engine or exhaust passages upstream of the NO_x absorbent 18. Therefore, when no air and fuel (or a combustible substance) is supplied in the exhaust passage upstream of the NO_x absorbent

18, the air-fuel ratio of the exhaust gas becomes the same as the operating air-fuel ratio of the engine (i.e., the air-fuel ratio of the air-fuel mixture supplied to combustion chambers of the engine).

When the NO_x absorbent is disposed in the exhaust passage of the engine, the NO_x absorbent actually performs the above-mentioned absorption and releasing operation of NO_x. Though the mechanism of this absorption and releasing operation of the NO_x absorbent is not clear at present, it is thought that the absorption and releasing operation is conducted by the mechanism shown in Figs. 4A and 4B. Figs. 4A and 4B explain the mechanism of the absorption and the releasing operation in the case where platinum Pt and barium Ba are carried on the carrier, as an example, but it is thought that a similar mechanism also applies if other precious metal, alkali metals, alkali earth metals, or rare earth metals are used.

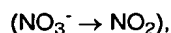
Namely, when the air-fuel ratio of the exhaust gas is lean, the concentration of oxygen in the exhaust gas becomes quite high. In this case, as shown in Fig. 4A, the oxygen O₂ is deposited on the surface of platinum Pt in the form of O₂⁻ or O²⁻. The NO in the exhaust gas reacts with O₂⁻ or O²⁻ on the surface of the platinum Pt and becomes



Then, a part of the produced NO₂ is oxidized on the platinum Pt and absorbed into the NO_x absorbent. While bonding with the barium oxide BaO, it is diffused in the absorbent in the form of nitric acid ions NO₃⁻ as shown in Fig. 4A. In this way, NO_x is absorbed in the NO_x absorbent.

As long as the oxygen concentration in the exhaust gas is high, the NO_x is produced on the surface of the platinum Pt, and as long as the NO_x is produced on the surface of the platinum Pt, and as long as the NO_x absorption capacity of the absorbent is not saturated, the NO_x is absorbed into the NO_x absorbent and nitric acid ions NO₃⁻ are produced.

On the other hand, when the oxygen concentration in the exhaust gas becomes low, the production of NO₂ is lowered and the reaction proceeds in an inverse direction



and thus nitric acid ions NO₃⁻ in the absorbent are released in the form of NO₂ from the NO_x absorbent. Namely, when the oxygen concentration of the exhaust gas flowing into the NO_x absorbent is lowered, absorbed NO_x is released from the NO_x absorbent. As explained in Fig. 3, the oxygen concentration in the exhaust gas decreases as the operating air-fuel ratio of the engine becomes lower. Therefore, even when the operating air-fuel ratio of the engine is lean compared to the stoichiometric air-fuel ratio, NO_x is released from the

NO_x absorbent when the air-fuel ratio of the exhaust gas approaches to the stoichiometric air-fuel ratio.

In this case, if the operating air-fuel ratio of the engine is rich compared to the stoichiometric air-fuel ratio, a relatively large amount of HC, CO are contained in the exhaust gas, and these components react with the oxygen O₂⁻ or O²⁻ on the platinum Pt and are oxidized. After oxygen O₂⁻ or O²⁻ on the platinum Pt are consumed by HC, CO in the exhaust gas, if HC and CO still remain in the exhaust gas, NO_x released from the NO_x absorbent as well as NO_x emitted from the engine are reduced by the HC and CO remaining on the platinum Pt. This oxidation of the HC and CO consumes the oxygen existing near the NO_x absorbent, and the concentration of oxygen in the atmosphere around the NO_x absorbent is lowered. Also, the NO₂ released from the NO_x absorbent reacts with the HC and CO in the exhaust gas as shown in Fig. 4B and is reduced to N₂. In this way, when the NO₂ on the surface of the platinum Pt reacts with HC and CO in the exhaust gas, and when the NO₂ no longer exists on the surface of the platinum Pt, the NO₂ is successively released from the absorbent. Accordingly, when HC and CO exist in the exhaust gas flowing into the NO_x absorbent, the NO_x is released from NO_x absorbent and quickly reduced to N₂.

In this case, the HC and CO in the exhaust gas immediately react with the O₂⁻ or O²⁻ on the platinum Pt and are oxidized, and subsequently if the HC and CO still remain after the O₂⁻ or O²⁻ on the platinum Pt are consumed, the NO_x released from the absorbent and the NO_x emitted from the engine are reduced.

The engine 1 in Fig. 1 is usually operated at a lean air-fuel ratio (for example, Kt = 0.7). Therefore, the NO_x emitted from the engine 1 is absorbed by the NO_x absorbent 18 during the usual operation. However, when the amount of NO_x accumulated in the NO_x absorbent increases, the NO_x absorbent is saturated with NO_x and the capability of the NO_x absorbent for absorbing NO_x falls. Further, when the amount of NO_x accumulated in the NO_x absorbent reaches the maximum amount of NO_x which the NO_x absorbent can hold (i.e., the NO_x saturating amount of the NO_x absorbent), the NO_x absorbent 18 cannot absorb NO_x in the exhaust gas any more, and NO_x emitted from the engine is directly released to the atmosphere.

Therefore, this embodiment detects the amount of NO_x absorbed in the NO_x absorbent 18 and operates the engine at a rich air-fuel ratio (for example, Kt = KK > 1.0) for a predetermined period CT₀ (Fig. 5) when the amount of NO_x absorbed in the NO_x absorbent increases to a predetermined value (i.e., a regenerating amount). This predetermined value is usually set at, for example, 70 to 80% of the maximum NO_x saturating amount, i.e., the NO_x absorbing capacity of the NO_x absorbent 18. By operating the engine at a rich air-fuel ratio, as explained above, NO_x absorbed in the NO_x absorbent is released, and reduced by HC and CO in the exhaust gas. Namely, in this embodiment, the

regenerating operation of the NO_x absorbent 18 is performed every time the amount of NO_x absorbed in the NO_x absorbent 18 reaches the regenerating amount.

Next, the method for detecting the amount of NO_x absorbed in the NO_x absorbent 18 will be explained. In this embodiment, the amount of NO_x absorbed in the NO_x absorbent 18 is detected indirectly by a calculation based on the engine load condition.

The amount of NO_x emitted from the engine per unit time changes in accordance with the engine load condition (such as Q/N and N). The amount of NO_x absorbed in the NO_x absorbent per unit time increases as the amount of NO_x emitted from the engine per unit time increases. Therefore, the total amount of NO_x absorbed by the NO_x absorbent can be calculated by adding the amount of NO_x emitted from the engine per unit time. In this embodiment, a NO_x counter CR is used as a parameter representing the amount of NO_x absorbed in the NO_x absorbent 18. The NO_x counter CR is obtained by adding the values of the amount of NO_x emitted from the engine 1 multiplied by a predetermined constant, as explained later.

Fig. 6 illustrates a typical change in the amount of NO_x emitted from an internal combustion engine in accordance with the change in the engine load condition. In Fig. 6, the vertical axis represents the amount of intake air per one revolution of the engine (Q/N) and the horizontal axis represents the engine speed (N). The curves show the amount of NO_x emitted from the engine per unit time. As seen from Fig. 6, the amount of NO_x emitted from the engine per unit time increases as the engine speed N increases when Q/N is the same, and also increases as Q/N increases when the engine speed N is the same. In this embodiment, the amount of NO_x emitted from the engine per unit time is determined by, for example, experiment in which the actual engine is operated under various load conditions, and stored in the ROM 32 of the control circuit 30 in the form of a numerical table based on Q/N and N similar to that in Fig. 2. During the engine operation, the control circuit 30 determines the amount of NO_x emitted from the engine from the numerical table periodically based on Q/N and N, and calculates the value of the NO_x counter CR by adding the values obtained by multiplying the values determined from the numerical table by a constant.

Fig. 7 shows a flowchart illustrating the operation for calculating the amount of NO_x absorbed in the NO_x absorbent 18 in this embodiment. This operation is performed by a routine executed by the control circuit 30 at predetermined intervals.

When the operation starts, in Fig. 7, at step 701, control circuit 30 reads the engine speed N and the amount of intake airflow Q from the sensors 23 and 13, respectively. At step 703, the amount of intake air per one revolution of the engine Q/N is calculated, and the amount KNO_x of NO_x emitted from the engine 1 per unit time is determined from the numerical table stored in the ROM 32 based on the calculated Q/N and N. The

value of the NO_x counter CR is obtained by adding the value of KNO_x at step 705.

Although the value of the NO_x counter CR is calculated based on the amount of NO_x omitted from the engine 1 per unit time, since the amount of NO_x absorbed in the NO_x absorbent increases as the engine operation time elapses, the value of the CR may be approximately determined by increasing the value of CR by a constant value at regular intervals.

In Fig. 8, at step 801, it is determined whether the regenerating operation of the NO_x absorbent 18 is required, i.e., whether the value of the NO_x counter CR has reached a predetermined value CR₀. The value CR₀ in this embodiment is, for example, set at a value between 70 and 80% of the maximum NO_x saturation amount KMAX, as explained later.

Fig. 8 shows a flowchart explaining the regenerating operation of the NO_x absorbent 18 in this embodiment. This operation is performed by a routine executed by the control circuit 30 at predetermined intervals.

If CR < CR₀ at step 801, since the amount of NO_x absorbed in the NO_x absorbent 18 is small and the regenerating operation thereof is not necessary, the operation immediately terminates after setting the value of a regeneration flag XF to 0 at step 803. When the value of the flag XF is set to 0, the value of correction factor Kt used in the fuel injection amount calculation is set to 0.7 and the engine 1 is operated at a lean air-fuel ratio. In this case, the NO_x absorbent 18 continues to absorb NO_x in the exhaust gas.

On the other hand, if CR ≥ CR₀ at step 801, since the amount of NO_x absorbed in the NO_x absorbent has increased, the operation proceeds to step 805 to set the value of the flag XF to 1. When the value of the flag XF is set to 1, the value of the correction factor Kt is set to KK. KK is a value larger than 1.0, and in this embodiment, the value of KK is set at about 1.04, therefore, when the correction factor Kt is set to KK at step 805, the operating air-fuel ratio of the engine 1 is shifted to a rich air-fuel ratio. Thus, exhaust gas with a rich air-fuel ratio flows into the NO_x absorbent 18, and the absorbed NO_x is released from the NO_x absorbent and reduced by HC, CO in the exhaust gas.

Steps 807 through 809 are the steps for terminating the regenerating operation. The regenerating operation in this embodiment terminates when a predetermined time has elapsed from the beginning of the regenerating operation. Namely, a time counter CT is increased by 1 at step 807 and, when the value of CT reaches a predetermined value CT₀ at step 808, the values of CT and CR are reset to 0. When the values of CR is set to 0, the operation executes step 803 after step 801 and, thereby, the value of the regeneration flag XF is set to 0 when the operation is next performed. Thus, the operating air-fuel ratio of the engine 1 is reset to a lean air-fuel ratio (Kt = 0.7) after the regenerating operation is performed for a period corresponding to the value CT₀ of the time counter. The value CT₀ is set at a value suffi-

cient for releasing the amount of NO_x corresponding to the value CR_0 of the NO_x counter from the NO_x absorbent 18. Since the value CT_0 varies depending on the type and size of the NO_x absorbent, the value CT_0 is determined by, for example, experiment using the actual NO_x absorbent.

By performing the operation in Fig. 8, since the regenerating operation is performed when the amount of NO_x absorbed in the NO_x absorbent reaches the predetermined regenerating amount, unreduced NO_x is never released from the NO_x absorbent during the engine operation. However, by the above operation, unreduced NO_x may be released from the NO_x absorbent after the engine has stopped if the engine is stopped when the amount of NO_x absorbed in the NO_x absorbent is relatively large. This problem will be explained in detail with reference to Fig. 9.

Fig. 9 illustrates the change in the maximum amount of NO_x held by the NO_x absorbent in accordance with the change in the temperature of the NO_x absorbent. The maximum amount which the NO_x absorbent can hold therein, i.e., the NO_x saturation amount changes in accordance with the temperature. The NO_x absorbent cannot hold an amount of NO_x in excess of the NO_x saturation amount determined by the temperature as shown in Fig. 9. The NO_x absorbent holds NO_x therein in the form of nitrate. Since the capacity of the NO_x absorbent for holding nitrate increases when the temperature is not very high, the NO_x saturation amount of the NO_x absorbent increases as the temperature increases in a relatively low temperature range. However, when the temperature further increases, nitrate held in the NO_x absorbent starts to decompose due to high temperature, and the NO_x saturation amount starts to decrease as the temperature increases. Therefore, the NO_x saturation amount reaches its maximum value (i.e., KMAX in Fig. 9) at a certain temperature. Usually, the NO_x absorbent is disposed in the exhaust gas passage at the position where the temperature of the NO_x absorbent becomes a temperature near the temperature at which the maximum NO_x saturation amount (KMAX in Fig. 9) is obtained (for example, 300 to 500°C) during the engine operation in order to fully utilize the capacity of the NO_x absorbent for absorbing NO_x .

The operation in Fig. 8 performs the regenerating operation when the amount of NO_x absorbed in the NO_x absorbent reaches the regenerating amount (the amount corresponding to the value of CR_0). Therefore, if the engine is stopped immediately before the amount of NO_x absorbed in the NO_x absorbent reaches the regenerating amount, the amount of NO_x corresponding to the regenerating amount remains in the NO_x absorbent after the engine has stopped. In this condition, if the NO_x absorbent is cooled after the engine has stopped, the amount of NO_x in excess of the NO_x saturation amount at the temperature of the NO_x absorbent after it is cooled is released. Since the atmosphere in the

exhaust gas passage and the NO_x absorbent is very lean (almost the same as the air-fuel ratio of the ambient air) when the engine is not operated, the NO_x released from the NO_x absorbent diffuses to the atmosphere without being reduced. The amount of unreduced NO_x released from the NO_x absorbent is expressed by ΔCR in Fig. 9, if the NO_x absorbent holds the amount of NO_x corresponding to CR_0 when the engine is stopped.

If the engine is restarted before the NO_x absorbent is cooled, unreduced NO_x is not released from the NO_x absorbent. However, in this case, the NO_x absorbent starts to absorb NO_x in the exhaust gas in the condition where a relatively large amount of NO_x is already held in the NO_x absorbent. Therefore, if the value of the NO_x counter CR is not retained until the engine is restarted, i.e., if the value of the NO_x counter is reset to its initial value 0 when the engine is restarted, the NO_x absorbent is easily saturated with the absorbed NO_x during the engine operation. This causes NO_x emitted from the engine to diffuse into the atmosphere without being absorbed by the NO_x absorbent.

Therefore, in this embodiment, the regenerating operation of the NO_x absorbent is performed when the engine is stopped in order to prevent the NO_x absorbent from releasing unreduced NO_x after the engine has stopped. By performing the regenerating operation when the engine is stopped, substantially no NO_x remains in the NO_x absorbent after the engine has stopped. Therefore, unreduced NO_x is not released from the NO_x absorbent even though the NO_x absorbent is cooled after the engine has stopped. Further, since the NO_x absorbent can start absorbing NO_x in the exhaust gas in the condition where no NO_x is held therein when the engine is next started, the accumulation of NO_x and resulting saturation of the NO_x absorbent during the engine operation can be avoided. Especially, this feature is advantageous when a NO_x absorbent having a very large NO_x absorbing capacity is used. If the NO_x absorbent having a NO_x absorbing capacity sufficiently large for absorbing and holding all the NO_x emitted from the engine during the whole operation, the regenerating operation during the engine operation is not required, and the regenerating operation can be performed only when the engine is stopped. Since the regenerating operation during the engine operation requires the operating air-fuel ratio of the engine to be shifted to a rich air-fuel ratio, fluctuation of the output torque of the engine and resulting deterioration of the driveability occurs. Therefore, if a NO_x absorbent having a large NO_x absorbing capacity is used, since the regenerating operation during the engine operation is not required, the deterioration of the driveability, or a worsening of the fuel economy due to frequent rich air-fuel ratio operation of the engine will not occur according to the present embodiment.

Fig. 10 is a flowchart illustrating an embodiment of the regenerating operation performed when the engine is stopped. This operation is performed by a routine

executed by the control circuit 30 at predetermined intervals.

In this embodiment, when the control circuit 30 determines that the engine is stopped, i.e., an engine stopping operation is performed by the operator of the engine (for example, when the ignition switch is turned off by the operator), it performs the regenerating operation of the NO_x absorbent by keeping the engine 1 running and shifting the operating air-fuel ratio of the engine to a rich air-fuel ratio until a predetermined time has elapsed.

Namely, at step 1001 in Fig. 10, it is determined whether an ignition switch of the engine is off and, if the ignition switch is on, the operation terminates immediately without performing steps 1003 through 1013.

If ignition switch is off at step 1001, the operation determines whether the ignition switch was off when the operation was last performed. If the ignition switch was on when the operation was last performed, this means that the operation is first performed after the ignition switch has been turned off. In this case, the operation resets a value of a time counter CST to 0 at step 1005 in order to measure the time elapsed after the ignition switch has been turned off before executing step 1007. If the ignition switch was off when the operation was last performed at step 1001, i.e., if the operation is not performed immediately after the ignition switch has been turned off, the operation directly proceeds to step 1007. CST is a counter increased by 1 at a second by a routine shown in Fig. 11, which is executed by the control circuit 30 at every one second. Therefore, after CST is reset to 0 at step 1005, the value of CST represents the time (seconds) elapsed after the ignition switch has been turned off.

At step 1007, it is determined whether a predetermined time CST₁ has elapsed since the ignition switch was turned off. If time CST₁ has not elapsed, i.e., if CST < CST₁ at step 1007, the operation terminates after setting the value of the regeneration flag XF to 1 at step 1009. If time CST₁ has elapsed, i.e., if CST ≥ CST₁ at step 1007, the operation executes step 1011 to reset the values of the regeneration flag XF and the NO_x counter CR to 0. After executing step 1011, the operation executes step 1013 to stop the operation of engine 1 by turning off a main relay. Namely, by executing steps 1007 through 1013, the engine is operated at a rich air-fuel ratio (XF = 1) until a predetermined time (CST₁) has elapsed since the engine stopping operation commenced (i.e., since the ignition switch was turned off) and is stopped when the predetermined time (CST₁) has elapsed. The time CST₁ is a time sufficient for releasing all the amount of NO_x from the NO_x absorbent even if the amount of NO_x corresponding to the value CR₀ of the NO_x counter is held in the NO_x absorbent. CST₁ is set at, for example, about 10 seconds in this embodiment, however, since the time CST₁ varies in accordance with the type and size of the NO_x absorbent, it is preferable to determine the time CST₁ by, for

example, experiment using the actual NO_x absorbent.

By the operation in Fig. 10, since substantially all the NO_x in the NO_x absorbent is released and reduced when the engine is stopped, unreduced NO_x is not released from the NO_x absorbent after the engine has stopped. Further, since the NO_x absorbent can start absorbing NO_x in the condition where no NO_x is held therein, the saturation of the NO_x absorbent with absorbed NO_x can be avoided during the engine operation.

Although the time CST₁ is set at a constant value in this embodiment, since the time required for regenerating the NO_x absorbent is shorter as the amount of NO_x held in the NO_x absorbent is smaller, CST₁ may be changed in accordance with the amount of NO_x absorbed in the NO_x absorbent when the engine is stopped. In this case, it is necessary to obtain the relationship between the amount of NO_x absorbed in the NO_x absorbent (i.e., the value of the NO_x counter CR) and the time (CST₁) required for regenerating the NO_x absorbent by, for example, experiment using the actual NO_x absorbent, and stores the required time CST₁ in the ROM 32 of the control circuit 30 as a numerical table using CR as a parameter. The required time CST₁ is determined from this numerical table using the value of the NO_x counter when the engine is stopped.

Further, as explained before, if the NO_x absorbing capacity of the NO_x absorbent is sufficiently large, the regenerating operation during the engine operation (Fig. 8) is not required.

Further, though the regenerating operation when the engine is stopped (Fig. 10) starts after the engine stopping operation (i.e., the turning off of the ignition switch) is commenced in this embodiment, the regenerating operation may be started before the engine stopping operation is commenced. In this case, for example, a manual switch for generating a signal for starting the regenerating operation is provided to the engine, and the operator starts the regenerating operation manually using this switch before turning off the ignition switch. In this case, the regenerating operation is also performed until the time CST₁ has elapsed regardless of whether or not the ignition switch is turned off after the regenerating operation is started.

Fig. 12 schematically illustrates the general configuration of another embodiment of the exhaust gas purification device according to the present invention.

In Fig. 12, reference numerals the same as those in Fig. 1 designate similar elements.

In Fig. 12, a reducing agent supply unit 120 is provided. The reducing agent supply unit 120 includes a gaseous reducing agent source such as a vessel 121 storing pressurized gaseous reducing agent and a nozzle 123 disposed in the exhaust gas passage 17 upstream of the casing 19 of the NO_x absorbent 18. A solenoid shut off valve 125 is provided on the conduit 127 connecting the nozzle 123 to the vessel 121. The solenoid shut off valve 125 opens and closes in accord-

ance with a signal supplied from the output port 36 of the control circuit 30 via a drive circuit 129.

In this embodiment, when the ignition switch is turned off, the engine operation is immediately terminated and the valve 125 is opened to supply gaseous reducing agent to the NO_x absorbent 18. The NO_x absorbent 18 is regenerated by the reducing agent instead of the rich air-fuel ratio exhaust gas from the engine in this embodiment. The reducing agent used in this embodiment can be any gas having a reducing ability (such as hydrogen, carbon monoxide, ammonia) or gaseous hydrocarbon (such as propane, propylene). According to this embodiment, the operation of the engine can be stopped immediately after the ignition switch is turned off.

The exhaust gas purification device includes a NO_x absorbent disposed in an exhaust gas passage of an internal combustion engine. The engine is mainly operated at a lean air-fuel ratio. The NO_x absorbent absorbs NO_x in the exhaust gas from the engine when the exhaust gas flowing into the NO_x absorbent is at a lean air-fuel ratio, and releases the NO_x absorbed therein and reduces it when the air-fuel ratio of the exhaust gas becomes a rich air-fuel ratio. A control circuit is provided for controlling the operating air-fuel ratio of the engine. When the ignition switch of the engine is turned off, the control circuit continues the engine operation for a predetermined period before terminating the engine operation. During this engine operation, the operating air-fuel ratio of the engine is controlled at a rich air-fuel ratio to supply exhaust gas with a rich air-fuel ratio to the NO_x absorbent. Therefore, NO_x absorbed and held therein when the ignition switch is turned off is released and reduced by the rich air-fuel ratio exhaust gas from the engine. Since the NO_x absorbent is maintained at the condition where no NO_x remains in the NO_x absorbent after the engine has stopped, unreduced NO_x is not released from the NO_x absorbent even if the NO_x absorbent is cooled after the engine has stopped.

Claims

1. An exhaust gas purification device for an internal combustion engine comprising:

a NO_x absorbent disposed in an exhaust passage of an internal combustion engine, said NO_x absorbent absorbs NO_x in the exhaust gas of the engine when the air-fuel ratio of the exhaust gas flowing into the NO_x absorbent is lean, and releases and reduces the absorbed NO_x when the air-fuel ratio of the gas flowing into the NO_x absorbent becomes rich; and a regenerating means for performing a regenerating operation which causes the NO_x absorbent to release and reduce the absorbed NO_x by supplying rich air-fuel ratio gas to the NO_x absorbent when the engine is stopped.

2. An exhaust gas purification device as set forth in claim 1, wherein said regenerating means starts the regenerating operation after an engine stopping operation is commenced.
3. An exhaust gas purification device as set forth in claim 2, wherein said regenerating means further performs the regenerating operation when a predetermined condition is satisfied during the engine operation.
4. An exhaust gas purification device as set forth in claim 3, further comprising NO_x amount detecting means for detecting the amount of NO_x absorbed in the NO_x absorbent, and wherein said regenerating means performs the regenerating operation when the amount of NO_x in the NO_x absorbent reaches a predetermined value during the engine operation.
5. An exhaust gas purification device as set forth in claim 2, wherein said regenerating means performs the regenerating operation by operating the engine at a rich air-fuel ratio for a predetermined period after the engine stopping operation is commenced.
6. An exhaust gas purification device as set forth in claim 5, further comprising NO_x amount detecting means for detecting the amount of NO_x absorbed in the NO_x absorbent and means for setting the length of the predetermined period in accordance with the amount of NO_x absorbed in the NO_x absorbent when the engine stopping operation is commenced.
7. An exhaust gas purification device as set forth in claim 5, wherein said regenerating means terminates the regenerating operation when substantially all of the NO_x absorbed in the NO_x absorbent is released from the NO_x absorbent and reduced.
8. An exhaust gas purification device as set forth in claim 2, wherein said regenerating means performs the regenerating operation by supplying a reducing agent to the NO_x absorbent for a predetermined period after the engine stopping operation is commenced.
9. An exhaust gas purification device as set forth in claim 8, further comprising NO_x amount detecting means for detecting the amount of NO_x absorbed in the NO_x absorbent and means for setting the length of the predetermined period in accordance with the amount of NO_x absorbed in the NO_x absorbent when the engine stopping operation is commenced.
10. An exhaust gas purification device as set forth in claim 8, wherein said regenerating means terminates the regenerating operation when substantially all of the NO_x absorbed in the NO_x absorbent

is released from the NO_x absorbent and reduced.

11. An exhaust gas purification device as set forth in claim 2, wherein said regenerating means terminates the regenerating operation when substantially all of the NO_x absorbed in the NO_x absorbent is released from the NO_x absorbent and reduced. 5
12. An exhaust gas purification device as set forth in claim 1, wherein said regenerating means further performs the regenerating operation when a predetermined condition is satisfied during the engine operation. 10
13. An exhaust gas purification device as set forth in claim 12, further comprising NO_x amount detecting means for detecting the amount of NO_x absorbed in the NO_x absorbent, and wherein said regenerating means performs the regenerating operation when the amount of NO_x in the NO_x absorbent reaches a predetermined value during the engine operation. 15 20

25

30

35

40

45

50

55

Fig. 1

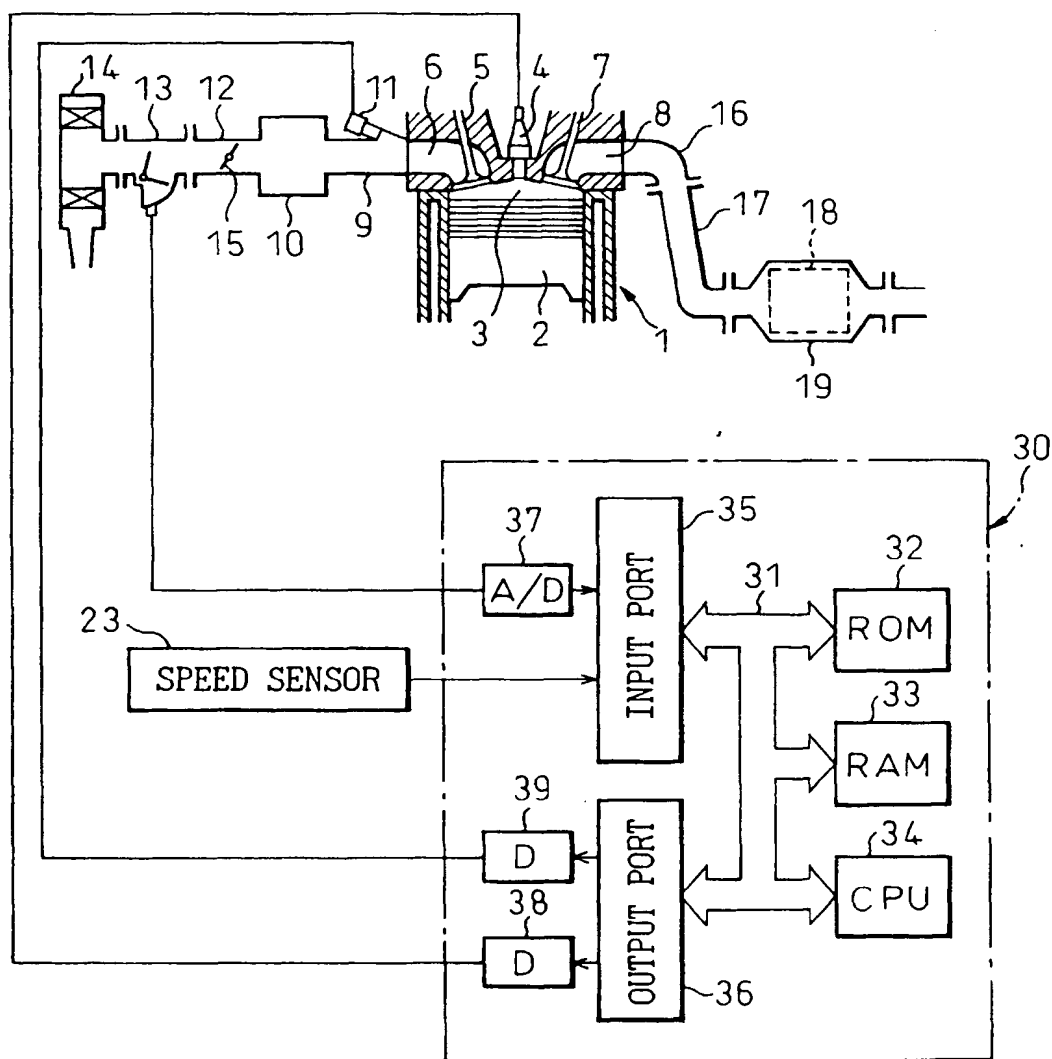


Fig.2

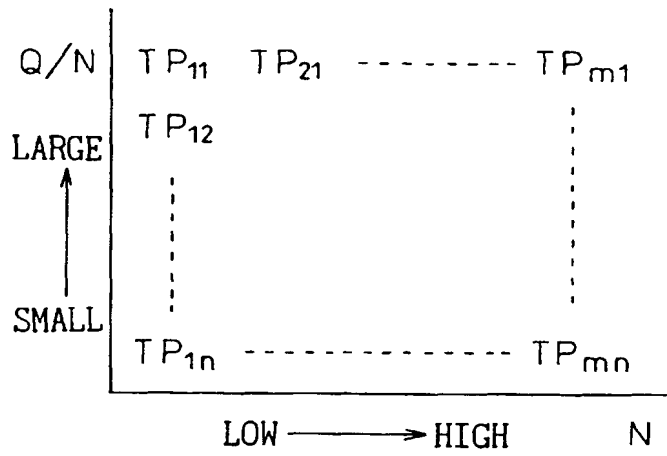


Fig.3

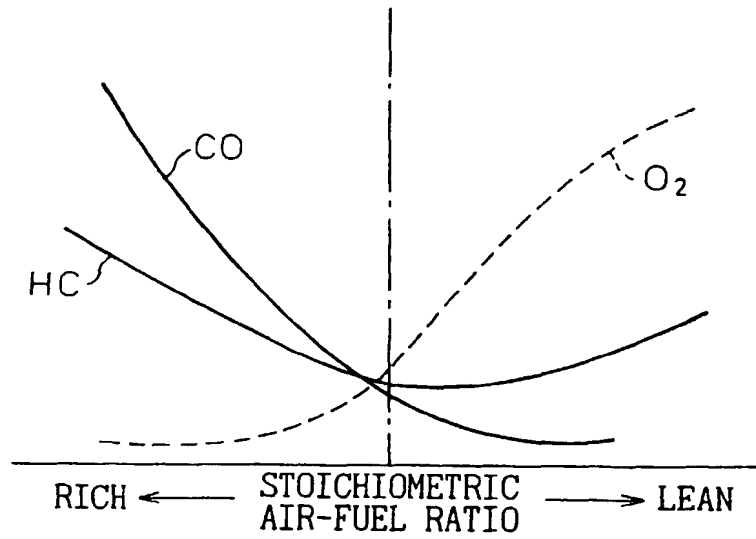


Fig.4A

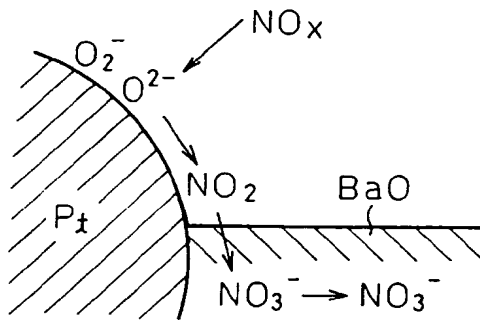


Fig.4B

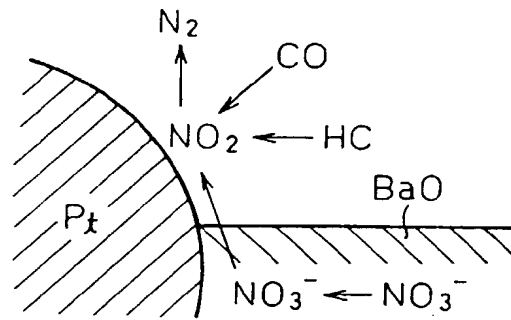


Fig.5

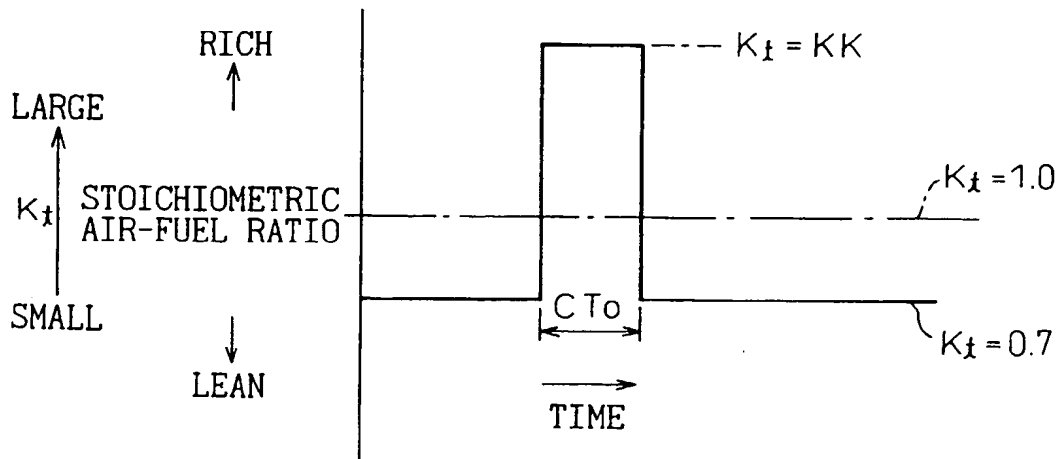


Fig.6

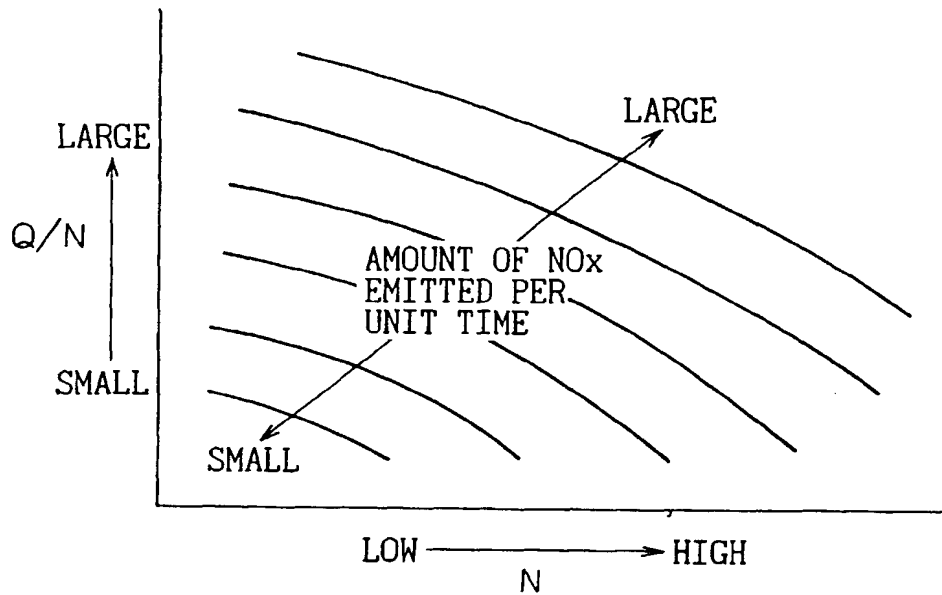


Fig.7

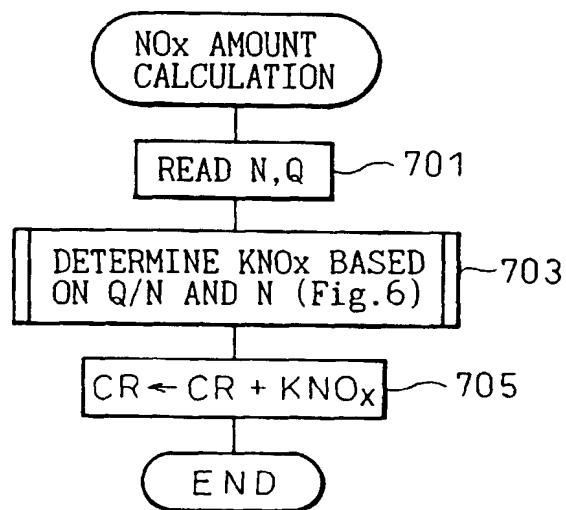


Fig.8

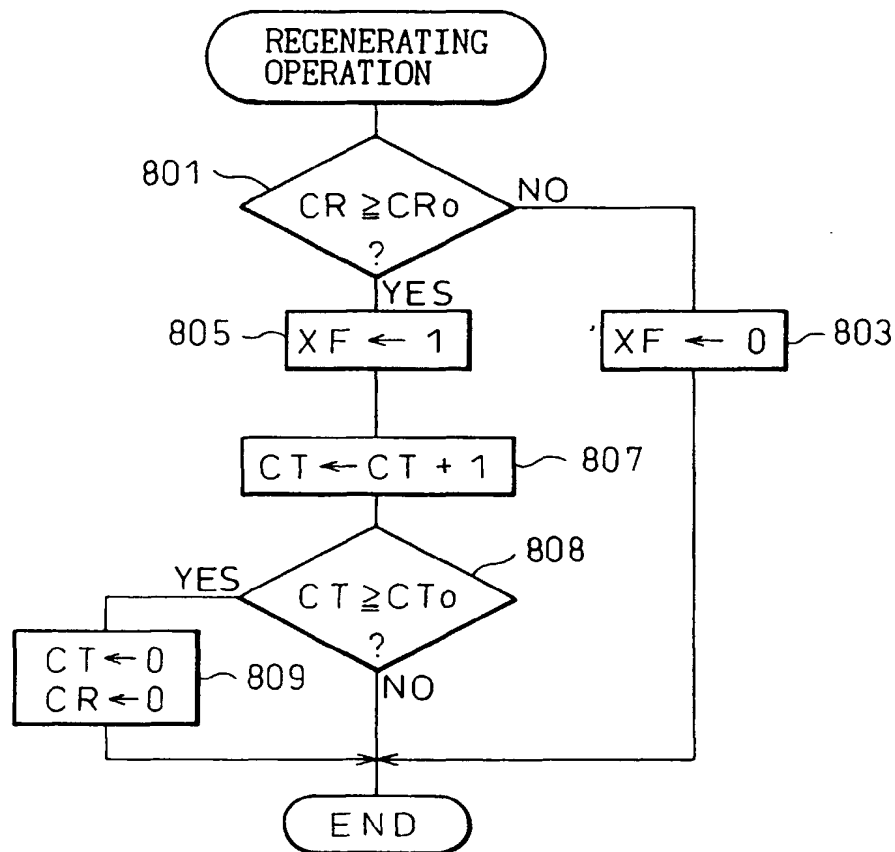


Fig.9

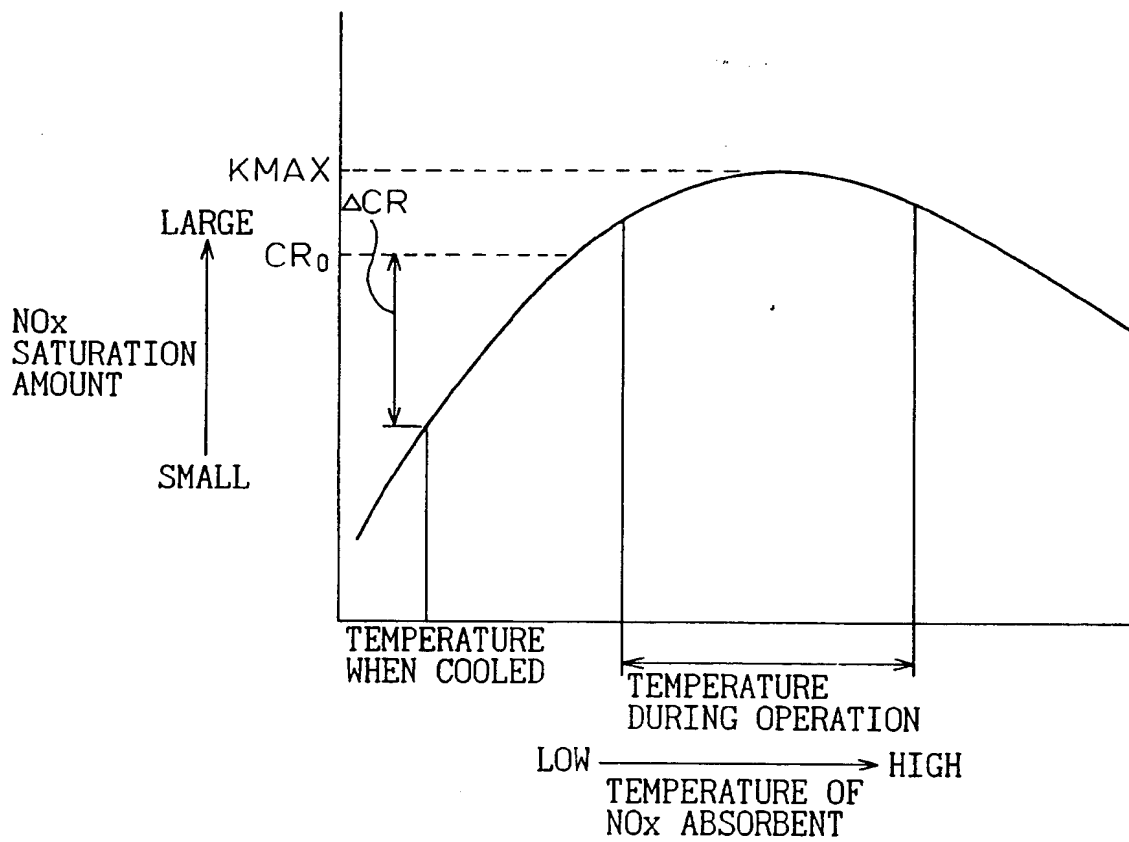


Fig.10

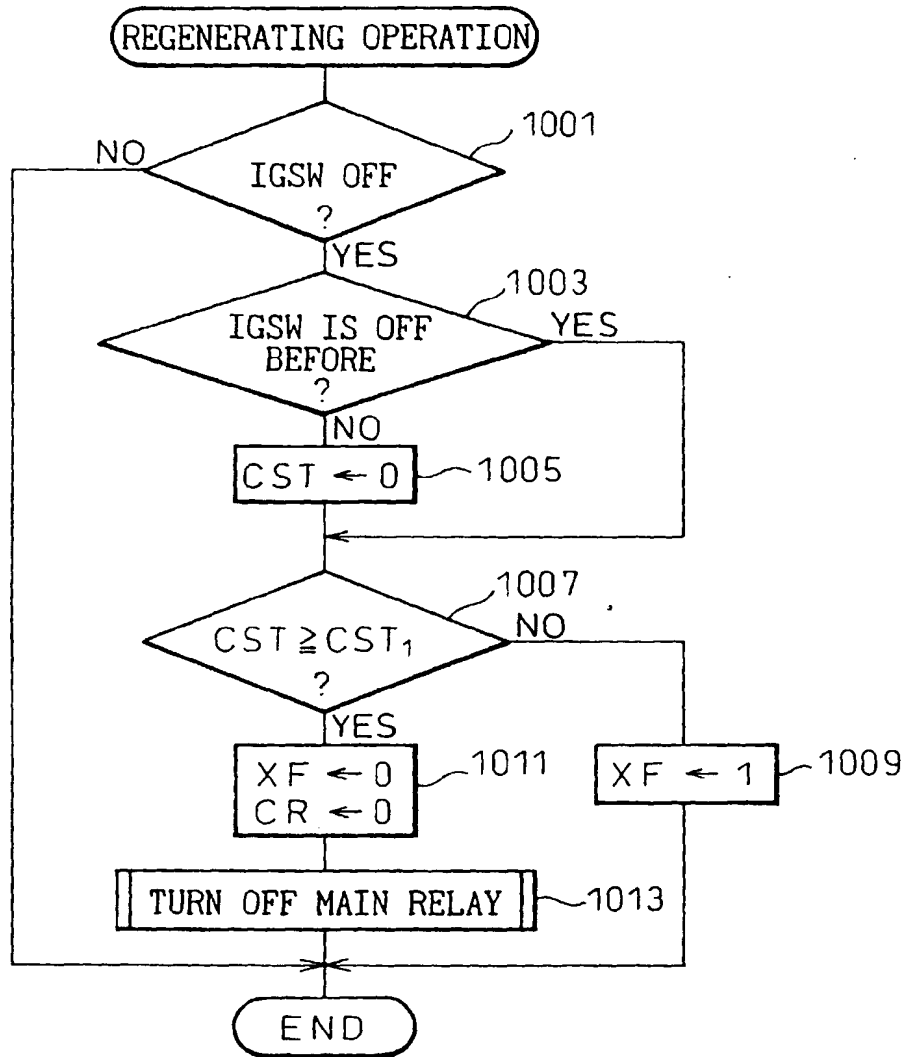


Fig.11

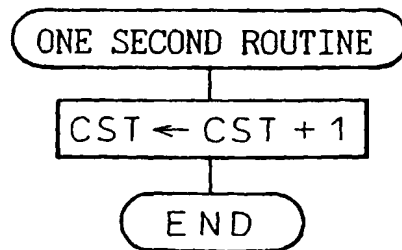
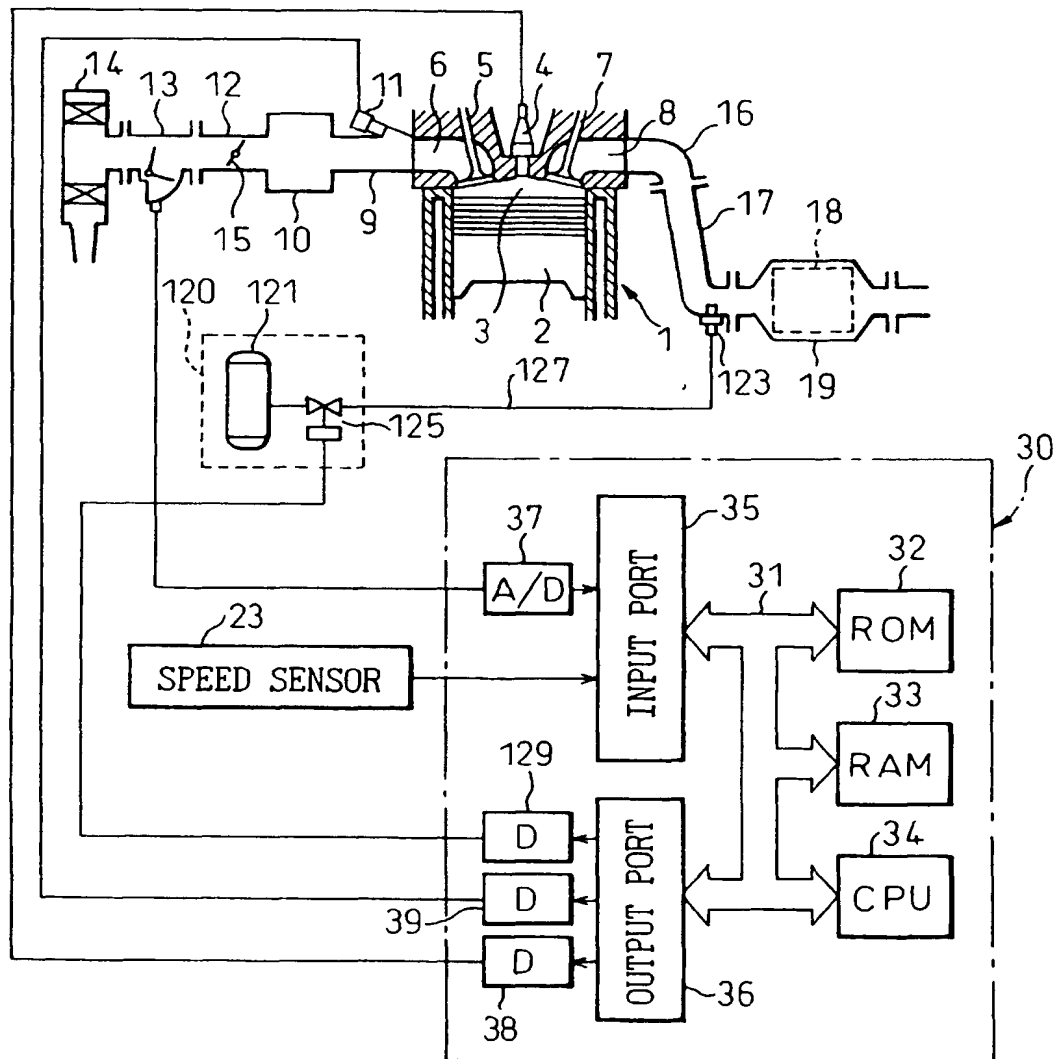
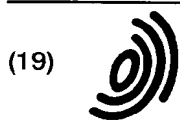


Fig.12





Europäisches Patentamt

European Patent Office

Office européen d s brevets



(11)

EP 0 869 267 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
22.12.1999 Bulletin 1999/51

(51) Int. Cl.⁶: F02D 41/14, F01N 3/08

(43) Date of publication A2:
07.10.1998 Bulletin 1998/41

(21) Application number: 98106083.3

(22) Date of filing: 02.04.1998

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 03.04.1997 JP 8529497

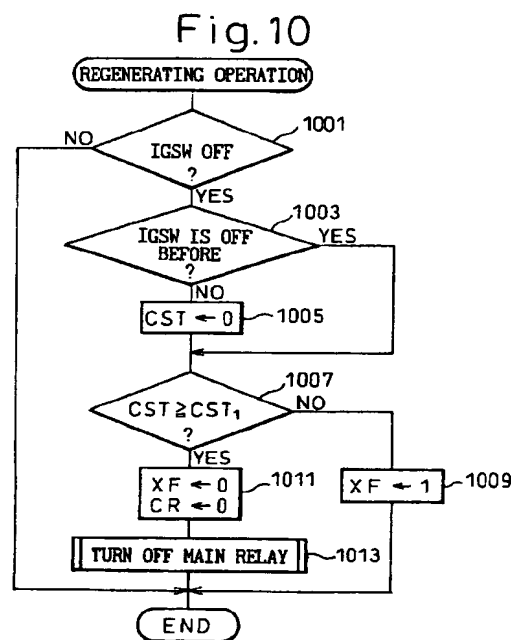
(71) Applicant:
TOYOTA JIDOSHA KABUSHIKI KAISHA
Aichi-ken 471-8571 (JP)

(72) Inventors:
• Gotoh, Masato
Toyota-shi, Aichi (JP)
• Katoh, Kenji
Toyota-shi, Aichi (JP)
• Asanuma, Takamitsu
Toyota-shi, Aichi (JP)

(74) Representative:
Leson, Thomas Johannes Alois, Dipl.-Ing. et al
Patentanwälte
Tiedtke-Bühling-Kinne & Partner,
Bavariaring 4
80336 München (DE)

(54) An exhaust gas purification device for an internal combustion engine

(57) The exhaust gas purification device includes a NO_x absorbent disposed in an exhaust gas passage of an internal combustion engine. The engine is mainly operated at a lean air-fuel ratio. The NO_x absorbent absorbs NO_x in the exhaust gas from the engine when the exhaust gas flowing into the NO_x absorbent is at a lean air-fuel ratio, and releases the NO_x absorbed therein and reduces it when the air-fuel ratio of the exhaust gas becomes a rich air-fuel ratio. A control circuit is provided for controlling the operating air-fuel ratio of the engine. When the ignition switch of the engine is turned off, the control circuit continues the engine operation for a predetermined period before terminating the engine operation. During this engine operation, the operating air-fuel ratio of the engine is controlled at a rich air-fuel ratio to supply exhaust gas with a rich air-fuel ratio to the NO_x absorbent. Therefore, NO_x absorbed and held therein when the ignition switch is turned off is released and reduced by the rich air-fuel ratio exhaust gas from the engine. Since the NO_x absorbent is maintained at the condition where no NO_x remains in the NO_x absorbent after the engine has stopped, unreduced NO_x is not released from the NO_x absorbent even if the NO_x absorbent is cooled after the engine has stopped.



EP 0 869 267 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 10 6083

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 747 581 A (JOHNSON MATTHEY PLC) 11 December 1996 (1996-12-11) * page 3, line 9 - line 12 * * figure 9 * * claims 1,3 *	1	F02D41/14 F01N3/08
A	--- PATENT ABSTRACTS OF JAPAN vol. 018, no. 360 (M-1634), 7 July 1994 (1994-07-07) & JP 06 093832 A (HITACHI LTD), 5 April 1994 (1994-04-05) * abstract *	1	
A	--- EP 0 702 134 A (TOYOTA MOTOR CO LTD) 20 March 1996 (1996-03-20) * column 6, line 22 - line 33 * * figures 1,4 *	1	
D,A	--- EP 0 598 917 A (TOYOTA MOTOR CO LTD) 1 June 1994 (1994-06-01) * column 12, line 2 - line 14 * * column 24, line 51 - column 25, line 1 * * column 25, line 40 - line 42 * * figures 12,13,23,24,26,27 *	1,3,4	TECHNICAL FIELDS SEARCHED (Int.Cl.6) F02D F01N
A	--- US 5 397 550 A (MARINO JR ROBERT R) 14 March 1995 (1995-03-14) * column 1, line 6 - line 10 * * column 3, line 29 - line 40 * * figure 1 *	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 1 November 1999	Examiner De Vita, D
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

EPO FORM 1503 03/02 (P4/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 10 6083

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

01-11-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0747581 A	11-12-1996	AU 705024 B	13-05-1999
		AU 5461496 A	19-12-1996
		AU 705112 B	13-05-1999
		AU 5842496 A	24-12-1996
		BR 9602640 A	08-09-1998
		BR 9606433 A	30-09-1997
		CA 2178274 A	07-12-1996
		CA 2196904 A	12-12-1996
		EP 0774054 A	21-05-1997
		WO 9639576 A	12-12-1996
		JP 9103645 A	22-04-1997
		JP 10504370 T	28-04-1998
		US 5776417 A	07-07-1998
		US 5939028 A	17-08-1999
JP 06093832 A	05-04-1994	NONE	
EP 0702134 A	20-03-1996	JP 8086213 A	02-04-1996
		DE 69510144 D	15-07-1999
EP 0598917 A	01-06-1994	DE 69326217 D	07-10-1999
		US 5437153 A	01-08-1995
		DE 69326417 D	21-10-1999
		EP 0598916 A	01-06-1994
		WO 9325805 A	23-12-1993
		WO 9325806 A	23-12-1993
		JP 2586739 B	05-03-1997
		US 5450722 A	19-09-1995
US 5397550 A	14-03-1995	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

THIS PAGE BLANK (USPTO)